

UCRL- 83366  
PREPRINT

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This Paper was Prepared for Submittal to  
Fourth ANS Topical Meeting,  
King of Prussia, Pennsylvania  
Oct. 14-17, 1980

April 23, 1980

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## PERMEATION OF TRITIUM THROUGH ALUMINUM WITH OXIDE FILMS

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## ABSTRACT

Models that explain transport of tritium through aluminum and oxide film were developed. We postulate that the  $OT^-$  ion is the rest state in the host lattice of the oxide film. The dominant method of transport is migration of  $T^+$  ion from one oxygen site to a neighboring oxygen site in the lattice. Immediately after transport,  $HTO$  is formed at the surface. Experiments were done by first loading air exposed aluminum to tritium followed by desorption. We measured the desorption rates with time. Diffusion coefficients at 300 K for the oxide are about  $10^6$  to  $10^7$  lower than for aluminum. About 98% of the gas released was tritiated water. Preliminary mathematical models based on atomic diffusion through the metal followed by ionic diffusion through the oxide seem to explain the desorption rates.

## INTRODUCTION

Aluminum and its alloys are considered immune to embrittlement when exposed to hydrogen. They also have a low permeability to hydrogen. These two properties make them attractive materials for tritium containment. At containment pressures up to 10 MPa, aluminum or its alloys can be structural materials. At higher pressures their use is restricted as bladders to prevent hydrogen contact with structural materials.

To insure containment of tritium, its permeation characteristics through containment materials must be determined under conditions realistic to the specific application. In many instances the permeation behavior is governed by the surface, while in others the permeation behavior is governed by bulk properties.

Published permeation constants<sup>1</sup> show a four hundred fold variation. This large range is attributed to experiments done with various surface effects which were not characterized or monitored.

All previous permeability measurements<sup>1</sup> of hydrogen or its isotopes in aluminum or its alloys can be conveniently placed into two categories, those with and those without surface

effects. The highest diffusivity measured is arbitrarily designated as being without surface effects. The others with surface effects are about  $10^4$  smaller, but dependent on surface treatment. Whenever a permeability measurement compares favorably with a previous result, it is assumed that the surface treatment was the same for both samples.

For assessment of tritium containment problems, we rely on the highest diffusivity values. In reality, these values are probably irrelevant to permeabilities of tritium through aluminum in most applications. Because permeability data with oxide films are not systematically characterized, we cannot make a realistic assessment of tritium containment problems. We are forced to assume worst case conditions; that is, those with the highest permeability.

Very few publications on hydrogen transport in non-metals are available. Fowler et al.<sup>2</sup> measured the diffusion of tritium in various forms of powdered  $Al_2O_3$  and single crystals of  $Al_2O_3$ . Their diffusion coefficients are about  $10^6$  to  $10^7$  lower than for aluminum metal. At 100°C, 95% of gas released was tritiated water, while at 700°C it decreased to 37%. The removal of water from the oxide before exposure to tritium did not change the value of the diffusion coefficient; thus they concluded that the diffusion of tritium atoms was the major mechanism of transport.

In previous studies<sup>1</sup> most hydrogen-aluminum permeability experiments were done with aluminum samples containing an oxide film. A few measurements, like those with tritium, minimized the contribution of the oxide film by mixing the samples with powdered LiD. The LiD reacted with the oxide film containing water, making highly permeable paths. Unfortunately, the measurements with tritium<sup>1</sup> did not identify the proportion of  $HTO$ ,  $HT$  or  $T_2$  that permeated.

The purpose of this study is to measure the solubility and diffusivity of tritium in aluminum and several commercial alloys with oxidized surface films in a temperature range 25-200°C and pressure range 10-100 MPa where measurements haven't been done before. The surface films will be characterized by Auger spectroscopy (AES), ion scattering spectrometry, and secondary ion mass spectrometry (SIMS).

"Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under contract number W-7405-ENG-48."

## EXPERIMENTAL PROCEDURE

Aluminum coupons (1/4 inch x 1 x 0.1 inch, 0.9999 purity) were used for the diffusion studies. The preliminary experiments were done with the oxide film formed at room temperature. The oxide film thickness was increased by exposing the coupons to powdered CuO at 240°C for about 100 hours. The coupons were saturated with tritium in the pressure range 100-1000 psia at room temperature. After exposure, the excess tritium was transferred to a uranium trap for storage. The samples were put in a second container for the gas evolution experiments.

The evolution of tritium from the coupons was monitored in the apparatus shown in Fig. 1. Argon flushed tritium away from the coupons through the ion chambers, panametric moisture probe, and molecular sieve dryer. The flow system was arranged so that the total tritium activity was measured in one ion chamber simultaneously with the moisture level by a Panametric probe in series with a molecular sieve dryer. The gaseous tritium activity is measured in a second ion chamber after the moisture (H<sub>2</sub>O and HTO) was removed.

The amount of tritium absorbed in the coupons was measured by first dissolving a sample (wt = 1 mg.) in 79% HNO<sub>3</sub> at 50°C, diluting by a fraction of  $2 \times 10^{-4}$ , then counting the radioactivity with a Beckman Model Betamate II liquid scintillation counter.

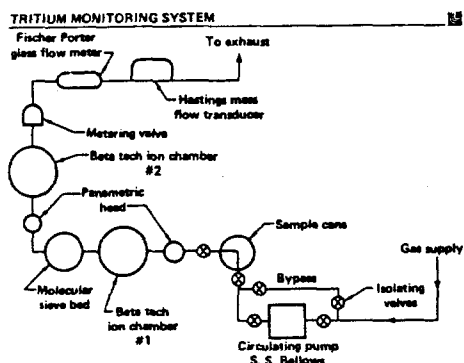


Fig. 1

## RESULTS AND DISCUSSION

### Absorption of Tritium

Aluminum forms a protective film of limiting thickness  $\sim 9\text{\AA}$  at room temperature when exposed to room air.<sup>3</sup> The protective film is Al<sub>2</sub>O<sub>3</sub> mixed with Al<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O. The amount of hydrate formed depends on the relative humidity during formation. The film protects aluminum from further oxidation, but not necessarily from other chemically active materials.

When Al<sub>2</sub>O<sub>3</sub> forms, it will attempt to conform to the Al lattice structure. Since the molar volume of Al<sub>2</sub>O<sub>3</sub> is about one-half the molar volume of Al, some cracks or pores can form to relieve tensile stresses at the interface.<sup>4</sup>

If the temperature is not increased, the layer thickness does not increase. If the temperature is increased, the limiting layer thickness increases, e.g., the layer increases to  $\sim 13\text{\AA}$  at 400°C. It is reasonable to assume that the protective oxide film absorbs and desorbs moisture readily. This moisture is loosely bound, perhaps in voids and cracks.

### Analysis of Desorption Data

The oxide appears to be de-coupled from the aluminum so that, for short times, i.e.,  $t \ll \frac{l^2}{\pi D}$ , where D is the diffusion coefficient and l is the sample thickness. The result is that for times up to about one-half of total gas evolved, we can approximate the evolution rates to be independent of the concentration of tritium at the Al-Al<sub>2</sub>O<sub>3</sub> interface. Thus, the rates are directly proportional to the amount absorbed by the oxide film.

The rate of loss of diffusing substance from a semi-infinite medium with zero surface concentration is given by

$$\frac{\partial Q}{\partial t} = \frac{D^{1/2} C_0}{\pi^{1/2} t^{1/2}} \quad (5)$$

Thus, plotting rate - vs -  $1/t$  produces a straight line and the diffusion constant D can be derived if the equilibrium concentration absorbed  $C_0$  is known.

Figure 1 shows an example of an experiment. The samples were cleaned in acetone, followed by an ethanol rinse before mixing with cupric oxide powder, and heated for about 100 hours at 400°C. We estimate that the oxidation increased the film thickness from  $\sim 9\text{\AA}$  to  $\sim 13\text{\AA}$ .

Table 1 compares our results with other published values. We conclude that diffusion of tritium out of the oxide film is the controlling method of transport.

There are two species, HTO and HT, of tritium that evolve from the samples. When the total activity is measured, 98.5% of the radioactivity is HT at the start, but it decreases to about 50% when 30% of the gases are evolved.

The amount of tritium absorbed by the samples was  $1.97 \times 10^{-3}$  cc/g (NTP), whereas the solubility of tritium in aluminum is estimated to be  $1.1 \times 10^{-9}$  cc/g (NTP). A factor of  $2 \times 10^6$  more tritium was absorbed by the samples than was expected for bulk aluminum. This large discrepancy can be explained by assuming that the amount of tritium absorbed is proportional to the amount of water in the oxide film.

TABLE I

COMPARISON OF DIFFUSION COEFFICIENTS OF TRITIUM IN ALUMINUM OXIDE AT 22°C

| Material  | D (cm <sup>2</sup> /s)  |                         | Temperature Range<br>of Measurement<br>(°C) |
|---|-------------------------|-------------------------|---|
|   | Upper Limit             | Lower Limit             |   |
| Al <sub>2</sub> O <sub>3</sub> Single Crystal                         | 2.1 x 10 <sup>-39</sup> | 7.8 x 10 <sup>-44</sup> | 600 - 1000                                  |
| Sintered Al <sub>2</sub> O <sub>3</sub>                               | 3.1 x 10 <sup>-31</sup> | 6.7 x 10 <sup>-36</sup> | 600 - 900                                   |
| Powdered Al <sub>2</sub> O <sub>3</sub><br>(condensibles not trapped) | 4.5 x 10 <sup>-21</sup> | 1.4 x 10 <sup>-32</sup> | 200 - 350                                   |
| Powdered Al <sub>2</sub> O <sub>3</sub><br>(condensibles trapped) (a) | 2.6 x 10 <sup>-27</sup> | 2.8 x 10 <sup>-29</sup> | 250 - 600                                   |
| Al with highly permeable<br>oxide film (b)                            | 2.4 x 10 <sup>-9</sup>  | -                       | 200 - 500                                   |
| Al with ~13 μm oxide film (c)   | 6.2 x 10 <sup>-26</sup> | -                       | 22°C  |

<sup>a</sup>The diffusion constants of tritium in the various forms of Al<sub>2</sub>O<sub>3</sub> were calculated from equations in reference (2).

<sup>b</sup>These permeability measurements were made with LiD in contact with the oxide film. The dehydrated oxide probably creates high permeability paths. The values were calculated by using equations reported in reference (1).

<sup>c</sup>This is our measurement. See Figure 2.

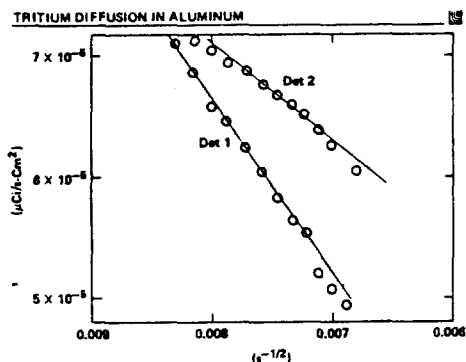


Fig. 2

#### Possible Transport Mechanism

There is evidence that T<sup>+</sup> and OT<sup>-</sup> are involved in tritium diffusion in oxides. Cathcart et al.<sup>6</sup> explain their diffusion measurements of tritium in TiO<sub>2</sub> by postulating that the dominant method of transport of tritium is the migration of T<sup>+</sup> ion

from one oxygen site (OT<sup>-</sup>) to a neighboring oxygen site in the host lattice. The experimental evidence for this mechanism is convincing. This mechanism of transport is consistent with our results, although more work is needed to verify it.

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but no extraneous groups like triphenylphosphine. Due to the concern for gettering tritium in air at very low concentrations we have designed and built a dynamic flow through getter system. Concentrations of approximately 1-10ppm  $T_2$  in air will be used to finally evaluate the performance of our best materials. Upon selection of the best material, investigation into the disposal of organic getters will begin. Butadiyne offers the possibility of cross-linking under tritium irradiation to form a strong unleachable plastic storage medium. Finally, pyrolysis studies will be conducted for the possible regeneration of  $T_2$ .

#### EXPERIMENTAL PROCEDURE

A weighed amount of getter material is placed in a 50cc glass reaction flask and attached to the vacuum manifold for hydrogen activation. The sample is pumped on for 30 minutes at  $10^{-3}$  torr. A pressure of hydrogen is then added to the sample to reduce 10% of the acetylene bonds. This "hydrogen activation" shortens the induction time of the reaction of tritium with the organic and is performed for all samples except the organometallics. When the pressure of hydrogen returns to zero the sample vessel is valved off, removed from the activation system, and attached to the getter system comprised of a copper manifold equipped with a 1000 torr baratron pressure transducer, a cryo-sorption roughing pump, a mechanical pump and a gas cylinder containing  $T_2$  in dry air. The system is pumped down to  $10^{-3}$  torr then leak checked with helium. A pressure of tritium feed gas is then added to the manifold so that when expanded into the sample vessel it will produce reaction pressures close to 1 atmosphere. When the expanded gas reaches equilibrium, the valve to the sample vessel is closed and the reaction is allowed to proceed at room temperature for 48 hours. The gas remaining in the manifold is then evacuated by a cryo-sorption pump. After 48 hours the sample vessel is removed from the system for mass spec analysis of the gas remaining.

The getter material is then placed in a 50cc glass column equipped with a coarse frit for support and a stopcock. The sample is first washed with 250cc of mixed solvent (90% methylene chloride, 10% diethyl ether) to dissolve and elute the organic getter. An aliquot of this solution is taken and the tritium is measured by liquid scintillation counting. The sample is dried with a stream of argon then washed with 100cc 2M HCl to elute the tritium in the aqueous phase. An aliquot of this solution is taken and counted. Because water is slightly soluble in the organic solvent determined to be optimum for dissolving the organic getter and because some color present in the acid wash indicated that some organic may be present in this phase an aliquot of both fractions is taken and washed to remove any HTO or  $T_2O$  present in the organic fraction and any organic in the acid fraction. The activity separated by these washes is then added to their respective fractions to yield the total amount activity in each phase. The firebrick substrate is dissolved in part by a solution of concentrated

hydrofluoric acid and nitric acid; an aliquot is taken and counted. The total activity found in each fraction is expressed as a mole percent of input tritium. The sum of these values in addition to the activity remaining in the gas phase gives the total closure number. Closure has varied from 11% to 100%. Low closure numbers may result from a loss of detectable tritium in the firebrick substrate as it is not completely dissolved by the HF and  $HNO_3$ . Gases evolved during the dissolving have been qualitatively shown to contain tritium. Work is planned to dissolve the substrate in a closed system and capture the gases evolved for mass spec analysis. Sorption of tritium into the glass of the reaction vessel has been investigated and found to be approximately 10% or less.

#### ACKNOWLEDGMENTS

We wish to thank Gene Nardella and Jack Baublitz of the Office of Fusion Energy, Department of Energy, for their support of this work.

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